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New method for determination of vaporization and sublimation enthalpy of aromatic compounds at 298.15 K using solution calorimetry technique and group-additivity scheme

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ABSTRACT

In this work a new method for determination of vaporization/sublimation enthalpies of aromatic compounds directly at $T = 298.15$ K was developed. This method is based on the general relationship between vaporization/sublimation enthalpy and enthalpies of solution and solvation of the studied compound in any solvent. According to this method the procedure for determination of vaporization (liquids) or sublimation (solids) enthalpy includes measurement of the solution enthalpy of the compound in a selected solvent and calculation of the solvation enthalpy for this system. A group-additivity scheme for calculation of solvation enthalpies is proposed. The solvation enthalpy of compound is estimated from the solvation enthalpy of parent aromatic or heteroaromatic compound and contributions of the substituent groups. Limiting solution enthalpies of 34 aromatic compounds (substituted benzenes, naphthalenes, biphenyls, pyrene, anthracene and pyridines) in carbon tetrachloride, benzene, acetonitrile and *N*,*N*-dimethylformamide were measured in the present work at 298.15 K. Vaporization/sublimation enthalpies of 78 aromatic and heteroaromatic compounds were determined directly at 298.15 K using experimentally measured solution enthalpies and predicted values of solvation enthalpies. The results are in good agreement with available literature data.

1. Introduction

Determination of thermodynamical functions of liquid–gas or solid–gas phase transitions is an important subject in chemical thermodynamics. The traditional way for evaluation of these values includes experimental studies of processes of transition from the condensed state to the gas phase usually at elevated temperatures. This procedure is not universal and has some well-known problems, which were discussed early [1,2]. Most critical of them are possible thermal instabilities of the compounds studied, significant effects of small amount of impurities on the experimental values and the ambiguity associated with extrapolation of thermochemical data from the temperature of measurements (T) to a reference temperature (298.15 K). Hence, the reliability of the vaporization/sublimation enthalpies obtained by conventional methods depends on the effect of each of these factors. In this regard, development of additional independent methods to assess phase transition enthalpies, which do not have the above-described problems, becomes a very important and useful task. First, these methods can help to resolve contradictions in existing literature data. Second, they can be applied to studies of low volatile and thermally unstable compounds, for which conventional methods are difficult or unusable. One possible way for development of such methods is application of solution calorimetry [3–8]. According to this approach vaporization (liquid solutes) or sublimation (solid solutes) enthalpies at 298.15 K can be determined from thermodynamic functions of solution ($\Delta_{soln}H^{A/S}$) and solvation ($\Delta_{solv}H^{A/S}$) of the studied compound in any solvent at 298.15 K by Eqs. (1) and (2):

$$\Delta_l^g H_m^A = \Delta_{soln}H^{A/S} - \Delta_{solv}H^{A/S} \quad (1)$$

$$\Delta_{cr}^g H_m^A = \Delta_{soln}H^{A/S} - \Delta_{solv}H^{A/S} \quad (2)$$

The enthalpy of solution required for application of Eqs. (1) and (2) can be measured experimentally by direct (solution calorimetry) or indirect (gas chromatography, solubility, etc.) techniques. The problem is how to obtain the enthalpy of solvation, because it can be measured experimentally only for gaseous compounds.

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